

12

AD-A181 550

DTIC FILE COPY

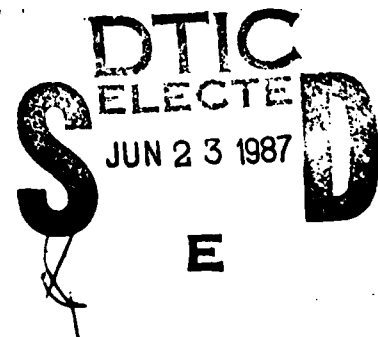


# DEVELOPMENT OF HIGH TEMPERATURE, IMPROVED PERFORMANCE POLYTHIOETHER SEALANTS, COATINGS AND ADHESIVES

Lester Morris, David A. Jordan, Melvin B. Young  
Products Research and Chemical Corporation  
P.O. Box 1800  
Glendale, CA 91509

JUNE, 1986

FINAL REPORT



*Approved for Public Release; Distribution Unlimited*

Prepared for  
Aircraft and Crew Systems Technology Directorate  
NAVAL AIR DEVELOPMENT CENTER  
Warminster, Pennsylvania 18974-5000

87 6 23 014

## NOTICES

**REPORT NUMBERING SYSTEM** - The numbering of technical project reports issued by the Naval Air Development Center is arranged for specific identification purposes. Each number consists of the Center acronym, the calendar year in which the number was assigned, the sequence number of the report within the specific calendar year, and the official 2-digit correspondence code of the Command Office or the Functional Department responsible for the report. For example: Report No. NADC-86015-70 indicates the fifteenth Center report for the year 1986 and prepared by the Systems and Software Technology Department. The numerical codes are as follows:

CODE	OFFICE OR DEPARTMENT
00	Commander, Naval Air Development Center
01	Technical Director, Naval Air Development Center
02	Comptroller
05	Computer Department
07	Planning Assessment Resources Department
10	Anti-Submarine Warfare Systems Department
20	Tactical Air Systems Department
30	Battle Force Systems Department
40	Communication & Navigation Technology Department
50	Mission Avionics Technology Department
60	Air Vehicle & Crew Systems Technology Department
70	Systems & Software Technology Department
80	Engineering Support Group

**PRODUCT ENDORSEMENT** - The discussion or instructions concerning commercial products herein do not constitute an endorsement by the Government nor do they convey or imply the license or right to use such products.

## REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS N/A	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution is unlimited	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) NADC-87071-60		5. MONITORING ORGANIZATION REPORT NUMBER(S) N/A	
6a. NAME OF PERFORMING ORGANIZATION Products Research and Chemical Corporation	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Naval Air Development Center	
6c. ADDRESS (City, State, and ZIP Code) 5430 San Fernando Road Glendale, CA 91209		7b. ADDRESS (City, State, and ZIP Code) Warminster, PA 18974	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Naval Air Development Center	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N62269-82-C-0370	
8c. ADDRESS (City, State, and ZIP Code) Warminster, PA 18974-5000		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO. 6276 IN	PROJECT NO. F61542
		TASK NO. F61-542-001	WORK UNIT ACCESSION NO. ZM 550
11. TITLE (Include Security Classification) Development of High Temperature, Improved Performance Polythioether Sealants, Coatings, and Adhesives (UNCLASSIFIED)			
12. PERSONAL AUTHOR(S) Lester Morris, David A. Jordan, Melvin B. Young			
13a. TYPE OF REPORT Final	13b. TIME COVERED FROM 9-82 TO 9-85	14. DATE OF REPORT (Year, Month, Day) June 30, 1986	15. PAGE COUNT
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			
<p>Fluid, heat, and electrical properties of polythioether formulations were measured. Effects of sulfur content, curing agents, and stabilizers on properties were examined for high temperature aircraft sealant development.</p> <p>A three to ten fold increase in retention of elastomeric properties at elevated temperatures to 400°F was observed versus current sealants.</p> <p>The materials' unique characteristics also suggest development of polythioether urethanes for fuel and fluid resistant coatings and lining, electrical sealants and anticorrosion barriers. (KEYWORDS)</p>			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Coleman Nadler		22b. TELEPHONE (Include Area Code) (215) 441-1898	22c. OFFICE SYMBOL 6062

FORWARD

This Final Report describes work by Products Research and Chemical Corporation during the period of September, 1982 to September, 1985 on Contract Number N62269-82-0370 "Development of High Temperature, Improved Performance Polythioether Sealants, Coatings and Adhesives" by the Naval Air Development Center (NADC), Warminster, Pennsylvania. Coleman Nadler was the NADC, technical monitor.

The program manager at Products Research and Chemical Corporation was Lester Morris. Laboratory research was conducted by David A. Jordan and Melvin B. Young.

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	



TABLE OF CONTENTS

	<u>Page</u>
I Introduction	1
II Summary	3
III Conclusions	4
IV List of Tables	7
V Discussion of Polymers	9
VI Formulation and Results	11
A. Water Resistance	30
B. Heat Resistance	30
C. Fuel Swell	30
VII Factors Influencing Electrical Resistance of Polythioethers in Aerospace Applications	31
VIII Urethane Elastomers as Fuel Tank Coatings	33
A. Physical Properties	33
B. Discussion of Factors Affecting Fuel Resistance	34
C. Effect of Sulfur Content on Fuel Resistant Mercaptan Terminated Polythioether	35
D. Water Resistance - Relation to Structure	36
IX Heat Resistance of Polythioethers	43
X List of Raw Materials and Suppliers	56

## 1. INTRODUCTION

Polysulfide based elastomeric compositions have been successfully used for many years in aircraft applications as fuel tank and pressurization sealants, fuel resistant electrical compounds and as environmental protective coatings.

These liquid polysulfide polymers contain formal and disulfide linkages along with mercaptan terminals which allow room temperature vulcanization by oxidizing agents.

The polysulfide polymers do show limitations. Repeating disulfide linkages restrict long term service temperatures to about 250°F and give only a few hours life at 360°F. Disulfide containing polymers undergo mercaptan attack in high sulfur fuels and normally show softening when confined in faying surfaces at elevated temperatures. Also, the alkaline oxidizing agents normally used in vulcanization encourage water absorption and softening.

The recent availability of high sulfur content polythioethers having monosulfide linkages in place of the disulfides, along with terminals allowing vulcanization by means other than oxidation suggested that higher heat and chemically resistant products could be obtained without sacrificing the good fuel and water resistance of polysulfide elastomers.

The current work examines the influence of curing agents and chemical variations of the polythioether backbone on thermal stability, fluid resistance, electrical resistance and physical properties, comparing the results with those obtained from standard commercial polysulfides. The ultimate goal is to develop formulations with improved performance in current and future aircraft and weapons systems.

## II SUMMARY

The fluid resistance, heat resistance, and physical properties of polythioethers with various sulfur contents cured by different mechanisms were determined in model formulations. The effect of sulfur content on the fuel and water resistance was examined. Factors influencing the electrical resistance of the polymers were briefly studied.

The characteristics of urethane containing polythioethers are presented and indicate that they are suitable as fuel resistant coatings and linings. Additives and curing agents were varied to determine their effects on thermal stability of formulations.

Investigation of factors influencing thermal stability were emphasized, resulting in formulations which showed both open and closed thermal stability significantly greater than that available with current commercial polysulfide formulations.



### III CONCLUSIONS

The properties of polythioethers with varying carbon/oxygen/sulfur ratios and cured by isocyanates, epoxies, acrylics and oxidation of mercaptan terminals shows that, compared to Thiokol polysulfide polymers, a large improvement in resistance to water swelling is observed with the greatest gain being found where the polymers consist of only sulfur, carbon and hydrogen. Fuel resistance is not greatly altered by changing the oxygen/sulfur ratio but decreases as the carbon content increases.

Thermal resistance of polythioether polymers, in terms of time of retention of properties at any temperature, is significantly better than polysulfides. The survival of polythioether is at least three times as long as polysulfides at a given temperature. Some formulations showed a ten-fold improvement in thermal resistance.

Cures based on manganese dioxide oxidation of the mercaptan are thermally inferior to those employing epoxy or acrylic cures.

Prolonged exposure at temperatures above 350°F results in surface hardening of sealant formulations examined. If oxygen is excluded, this surface effect is eliminated and elastomeric properties remain for more than one week at 360°F and 24 hours at 400°F. Otherwise, surface hardening occurs in about one half this period. Formulations have been made which pass many of the requirements of MIL-S-8802 and MIL-S-83430, utilizing test temperatures 100°F higher than specification testing requires.

Electrical properties of polythioether urethanes are approximately equal to those of polyether urethanes providing the catalyst used in the polymerization is removed. Polythioether urethanes have significantly improved water and fuel resistance compared to polyether urethanes.

The fluid resistance, heat resistance and physical properties of polythioethers with 29% sulfur cured by different mechanisms were determined, in model formulations. Manganese dioxide cures show inferior water resistance to epoxy and acrylic cures. Fuel resistance is not greatly influenced by the curing agent. Urethane containing polymer is better in fuel resistance than without urethane.

The characteristics of urethane containing polythioethers show that they have application as fuel resistant coatings and linings. Additives and curing agents were varied to determine their effects on thermal stability of formulations. Anticorrosive fuel resistant primers and coatings are also candidates for development.

The properties of the polythioethers also suggest their use in electrical potting and molding compositions where good fuel resistance is expected. Sonar devices using castor oil and urethane components could benefit from polythioether based urethanes.

Flexible coating materials with superior fluid, and thermal resistance along with corrosion inhibitive properties appear to be another potential area for development.

Conductive sealants with elevated temperature resistance to withstand composite processing conditions suitable for fileting and faying surfaces also have potential. The conductive sealants can also be provided with inhibitors to prevent galvanic attack between metals and carbon fiber reenforced composites.

Investigation of factors influencing thermal stability were emphasized in this work resulting in formulations which showed 3 to 10 times longer retention of elastomeric properties, than is available with current commercial polysulfide formulations in both open and closed configurations at 310°F to 400°F.

## List of Tables

<u>Table</u>		<u>Page</u>
I	Comparison of Initial Properties of a Commercial Polysulfide with Various Cures of Polythioethers (29% S)	13
II	Comparison of Fuel Resistance JRF at 140°F	14
III	Water Resistance at 140°F	15
IV	Heat Resistance at 275°F - 3 days	16
V	Heat Resistance at 275°F - 7 days	17
VI	Heat Resistance at 300°F - 1 day	18
VII	Heat Resistance at 300°F - 3 days	19
VIII	Heat Resistance at 360°F - 1 day	20
IX	Heat Resistance at 360°F - 3 days	21
X	Change in Properties of MIL-S-83430 B-1/2 (63A) After Various Exposures	22
XI	Changes in Properties of Polythioether/Alkaline Manganese with Phenolic (63C) After Various Exposures	23
XII	Changes in Properties of Polythioether Non-Alkaline Manganese (74D)	24
XIII	Change in Properties of Polythioether Scavenged Non-Alkaline Manganese (74C) After Various Exposures	25
XIV	Change in Properties of Polythioether Epoxy Cure with Phenolic (63D)	26
XV	Change in Properties of Polythioether Epoxy Cure with Phenolic (63B) After Various Exposures	27
XVI	Change in Properties of Polythioether Alkaline Manganese (74B) After Various Exposures	28
XVII	Change in Properties of Polythioether Scavenged Alkaline Manganese Cure (74A) After Various Exposures	29

<u>Table</u>		<u>Page</u>
XVIII	Comparison of JRF Resistance in Relation to Composition of Backbone	36
XIX	Comparison of Water Resistance in Relation to Composition of Backbone	37
XX	Tabulation of the Chemical Resistant Properties of Model Formulations of Sulfur Containing Polymers	38
XXI	Table Comparing Fuel, Water, and Heat Resistance of Permapol Polymers and Thiokol	39
XXII	Table Comparing Resistance of MnO <sub>2</sub> Cured and Peroxide Cured P-3 (29)	40
	TGA Graph of Polysulfide Sealant and Permapol P-3 Sealant	42
XXIII	Comparison of Resistance of Acrylic Cures of Polythioether and Standard Polysulfide	45
XXIV	Effect of Additives on Weight Loss of Uncured 43% S Material Heated 24 Hours at 360°F	46
XXV	Weight Loss of Permapol P-3 (43% S) Cured with Trimethylol Propane Triacrylate and Various Additives	47
XXVI	Comparison of Acrylic Cured Thiokol with Polythioether in Weight Loss at 360°F	48
XXVII	Tabulation of Formulations Cured with Acrylates	49
XXVIII	Effect of Heating at 400°F for 8 Hours on Lap Shear Values of Thiokol and P-3 (29) Based Sealants	49
XXIX	Formulations Examining Effect of Ferrocene and Aluminum on Lap Shear Strength at 400°F	50
XXX	Comparison of Formulated Permapol P-3 (29% S) Weight Losses at 360°F	51
XXXI	Effect of Pigmentation on Physical Properties Initially and After Exposure at 360°F	52
XXXII	Effect of Pigmentation and Stabilizers on Heat and Fluid Resistance of Model Formulas	53
XXXIII	Effect of Crosslinking on Thermal and Fuel Resistance of Polythioether	54

V DISCUSSION OF POLYMERS

The basic polymers produced for this program were synthesized by condensation of selected beta thioalcohol monomers according to U.S. Patent 4,366,307 and patents pending.

The sulfur content of the polymers varies from 24% to 49% depending upon the ratio of mercaptan or thioether to alcohol groups used in the condensation. Terminal hydroxyl groups may be used in isocyanate cures or they may be converted to mercaptan terminals by adding diisocyanate and then allyl alcohol followed by addition of a dimercaptan to the isocyanate terminated polythioether polyol in accordance with U. S. patent 3,923,748. Such mercaptan terminated polymers in the program are designated with the letter "U". Thus P-3.8U is a mercaptan terminated polythioether containing urethane groups.

Mercaptan terminated polythioethers without urethane groups are prepared by cocondensing a beta-thio-unsaturated alcohol and beta-thio-glycols as described in U.S. patent 4,366,307 followed by addition of dimercaptan to the resulting terminal double bonds.

The polymer backbone from the condensation is represented as:



In order to insure liquidity of the polymers some pendant methyl groups are included and are obtained by inclusion of secondary beta-thio-glycols in the condensation reaction. Typically, about 20% of the alcohol groups are secondary.

The term "scavenged" is used in the description of some of the thioether polymers. These are mercaptan terminated polythioethers with very small amounts (on the order of 1%) of diisocyanate incorporated to insure that no residual acid or hydroxy groups will be present in the structure.

#### IV. FORMULATION AND RESULTS

##### Evaluation of 29% Sulfur Material

Initial evaluation of physical and chemical properties was conducted with a polythioether polymer having 28-29% sulfur. The control material was a two component aircraft sealant qualified to MIL-S-83430 and based upon a Thiokol polysulfide polymer which uses manganese dioxide as the curing agent.

Initial curing agents examined for the thioether were manganese dioxide and epoxy resin. It was found that the compatibility of oxygen free polythioethers with standard bisphenol epoxy resins was very poor so that well cured materials were not obtained for testing. The functionality of the polymer was about 2.5 with a number average molecular weight of 5,000 as determined by gel permeation chromatography. All polymers were mercaptan terminated. Cured 1/8" sheets of each formulation were measured for physical properties before and after exposure to heat, water and JRF.

A series of formulations based upon the manganese dioxide and epoxy cure of Permapol P-3 (29% S) were examined for heat, fuel and water resistance as shown in the accompanying tables, I thru XVII. The units in which the values shown in the tables are expressed are as follows:

Hardness - Shore Durometer A

Die B Tear Strength - pounds per square inch

Tensile Strength - pounds per square inch

Elongation - percent increase in length at ultimate elongation.



Formulations

<u>Base</u>	<u>63A</u>	<u>63B</u>	<u>63C</u>	<u>63D</u>	<u>74A</u>	<u>74B</u>	<u>74C</u>	<u>74D</u>
Permapol® P-3.8U	-	-	100	-	-	-	-	-
Permapol P-3.8	100	100	-	-	100	-	100	-
Permapol P-3.8 Scavenged	-	-	-	100	-	100	-	-
Calcium Carbonate	50	50	50	50	50	50	50	50
Methylol Phenol (GE75108)	5	5	5	-	-	-	-	-
2,4,6 tri-dimethyl Amino Methyl Phenol (DMP-30)	1.5	-	1.5	-	-	-	-	-
Toluene	10	10	5	10	10	10	10	10
<u>Accelerator</u>								
Permapol Polythioether Plasticizer	-	3.23	-	3.23	3.23	10	10	-
Manganese Dioxide PH 10.2	-	5.60	-	5.60	5.60	-	-	-
Calcium Carbonate	-	0.17	-	0.17	0.17	-	-	-
Epoxy Novolac Dow DEN 431	11	-	11	-	-	-	-	-
Manganese Dioxide (fine ore)	-	-	-	-	-	10	10	-

Standard MIL-S-83430 Material

TABLE I  
COMPARISON OF INITIAL PROPERTIES OF A COMMERCIAL  
POLYSULFIDE WITH VARIOUS CURES OF POLYTHIOETHERS (29% S)

<u>Material</u>	<u>HARDNESS</u>	<u>DIE B TEAR STRENGTH</u>	<u>TENSILE STRENGTH</u>	<u>ELONG.</u>
MIL-S-83430 R 1/2 63A	58	80	388	333
P.3.8 Epoxy Cure + phenolic 63B	50	41	392	200
P.3.8 Alkaline Manganese with phenolic 63C	25	52	245	700
P.3.8 U Epoxy Cure with phenolic 63D	43	62	438	350
P.3.8 Scavenged Alkaline Manganese 74A	56	47	360	120
P.3.8 Standard Alkaline Manganese 74B	32	47	272	400
P.3.8 Scavenged Non-Alkaline Manganese 74C	52	40	310	135
P.3.8 Standard Non-Alkaline Manganese 74D	29	31	267	400

TABLE II  
COMPARISON OF FUEL RESISTANCE  
After 7 days of Immersion in JRF @ 140°F

MATERIAL	% SWELL	HARDNESS	% SOFTENING	TEAR STRENGTH	% CHANGE	TENSILE STRENGTH	% DECREASE	ELONG.	% CHANGE
MIL-S-83430 B 1/2 63A	5.7	38	35	60	25	220	43	425	+28
P.3.8 Epoxy cure with phenolic 63B	15	31	38	16	61	180	54	170	-15
P.3.8 Alkaline manganese with phenolic 63C	17	13	48	42	19	122	50	370	-47
P.3.8 U Epoxy cure with phenolic 63D	9.4	18	58	38	39	200	54	460	+28
P.3.8 Scavenged alkaline manganese 74A	16	41	27	17	-64	151	58	113	-6
P.3.8 Standard alkaline manganese 74B	18	14	56	18	-62	100	63	307	-23
P.3.8 Scavenged non-alkaline manganese 74C	14	39	25	18	-55	150	52	130	-4

NADC-87071-60

TABLE III  
WATER RESISTANCE  
After 7 days of exposure at 140°F

MATERIAL	% WEIGHT CHANGE	HARDNESS	DIE B		TEAR STRENGTH	% TEAR STRENGTH CHANGE	TENSILE STRENGTH	% TENSILE STRENGTH CHANGE	ELONG.	% ELONG. CHANGE
			% HARDNESS CHANGE	CHANGE						
MIL-S-83430 B 1/2 63A	+9.6	43	-26		64	-20	209	-46	360	+7.5
P.3.8 Epoxy cure with phenolic 63B	+3.4	42	-16		50	+22	214	-45	170	-15
P.3.8 Alkaline manganese with phenolic 63C	+20	23	-8		56	+7	165	-33	460	-35
P.3.8 U Epoxy cure with phenolic 63D	+3.8	25	-42		54	-13	285	-35	500	+43
P.3.8 Scavenged alkaline manganese 74A	+15	43	-23		45	-4	251	-30	183	+52
P.3.8 Standard alkaline manganese 74B	+24	17	-47		25	-47	100	-63	415	+4
P.3.8 Scavenged non-alkaline manganese 74C	+7	46	-12		45	+13	260	-16	225	+67

TABLE IV  
HEAT RESISTANCE AT 275°F  
After 3 days exposure

MATERIAL	% WEIGHT CHANGE	HARDNESS	DIE B % HARDNESS CHANGE	TEAR STRENGTH	% TEAR STRENGTH CHANGE	TENSILE STRENGTH	% TENSILE STRENGTH CHANGE	ELONG.	% ELONG. CHANGE
MIL-S-83430 B 1/2 63A	-6	78	+35	92	+15	456	+18	160	-52
P.3.8 Epoxy cure with phenolic	-1.8	53	+6	25	-39	311	-21	105	-48
P.3.8 Alkaline manganese with phenolic	-2	33	+32	46	-12	287	+17	260	-63
P.3.8 U Epoxy cure with phenolic	-2.9	43	0	21	-66	308	-30	100	-71

NADC-87071-60

TABLE V  
HEAT RESISTANCE AT 275°F  
After 7 days of exposure

MATERIAL	% WEIGHT CHANGE	HARDNESS	% HARDNESS CHANGE	DIE B TEAR STRENGTH	% TEAR STRENGTH CHANGE	TENSILE STRENGTH	% TENSILE STRENGTH CHANGE	ELONG.	% ELONG. CHANGE
MIL-S-83430 B 1/2 63A	-8	69	+19	80	0	443	+14	75	-78
P.3.8 Epoxy cure with phenolic 63B	-2.0	54	+8	26	-37	250	-36	60	-70
P.3.8 Alkaline manganese with phenolic 63C	2.6	37	+48	38	-27	219	-10	150	-79
P.3.8 U Epoxy cure with phenolic 63D	3.4	52	+21	19	-69	249	-41	50	-86
P.3.8 Scavenged alkaline manganese 74A	-22	48	-15	52	+11	340	-6	140	+14
P.3.8 Standard alkaline manganese 74B	-2.2	34	+6	42	-11	275	+1	240	-40
P.3.8 Scavenged non-alkaline manganese 74C	1.9	36	-31	44	+10	228	-26	225	+67

NADC-87071-60

TABLE VI  
HEAT RESISTANCE AT 300°F  
After 1 day of exposure

MATERIAL	% WEIGHT CHANGE	HARDNESS	% HARDNESS CHANGE	DIE B TEAR STRENGTH	% TEAR STRENGTH CHANGE	TENSILE STRENGTH	% TENSILE STRENGTH CHANGE	ELONG.	% ELONG. CHANGE
MIL-S-83430 B 1/2 63A	-6.2	68	+17	77	-4	457	+18	192	-42
P.3.8 Epoxy cure with phenolic	-1.7	51	+2	21	-50	313	-20	125	-38
P.3.8 Alkaline manganese with phenolic	-2.1	30	+20	51	-0.5	280	+14	325	-54
P.3.8 U Epoxy cure with phenolic	2.5	47	+9	16	-74	230	-48	90	-74

NADC-87071-60

TABLE VI I  
HEAT RESISTANCE AT 300°F  
After 3 days of exposure

MATERIAL	% WEIGHT CHANGE	HARDNESS	% HARDNESS CHANGE	DIE B TEAR STRENGTH	% TEAR STRENGTH CHANGE	TENSILE STRENGTH	% TENSILE STRENGTH CHANGE	ELONG.	% ELONG. CHANGE
MIL-S-83430 B 1/2 63A	-10.8	78	+34	78	-3				
P.3.8 Epoxy cure with phenolic 638	-2.2	53	+6	16	-61				
P.3.8 Alkaline manganese with phenolic 63C	-2.75	38	+52	45	-13				
P.3.8 U Epoxy cure with phenolic 63D	-3.9	57	+25	17	-73	251	-43	50	-86

NADC-87071-60



TABLE VIII  
HEAT RESISTANCE AT 360°F  
After 1 day of exposure

MATERIAL	% WEIGHT CHANGE	HARDNESS	% HARDNESS CHANGE	DIE 8 TEAR STRENGTH	% TEAR STRENGTH CHANGE	TENSILE STRENGTH	% TENSILE STRENGTH CHANGE	ELONG.	% ELONG. CHANGE
MIL-S-83430 B 1/2 63A	-21	92	+59	( 100 BRITTLE TO TEST )					
P.3.8 Epoxy cure with phenolic 63B	-3.8	63	+26	( 100 BRITTLE TO TEST )					
P.3.8 Alkaline manganese with phenolic 63C	-5	42	+68	32	-39	71	71	50	93
P.3.8 Scavenged alkaline manganese 74A	-5	43	-23	39	-17	71	-80	50	-58
P.3.8 Standard alkaline manganese 74B	-4.3	29	-9	+	+	+	+	+	+
P.3.8 Scavenged non-alkaline manganese 74C	-5	29	-44	19		50	-84	50	63
P.3.8 Standard non-alkaline manganese 74D									

specimens flowed, became thermoplastic

+Specimens stretched out during exposure - Not testable.

TABLE IX  
HEAT RESISTANCE AT 360°F  
After 3 days of exposure

MATERIAL	% WEIGHT CHANGE	HARDNESS	% HARDNESS CHANGE	DIE B TEAR STRENGTH	% TEAR STRENGTH CHANGE	TENSILE STRENGTH	% TENSILE STRENGTH CHANGE	ELONG.	% ELONG. CHANGE
MIL-S-83430 B 1/2 63A	*	*	*	(	TOO BRITTLE TO TEST	)			
P.3.8 Epoxy cure with phenolic 63B	-7.8	75	+50	(	TOO BRITTLE TO TEST	)			
P.3.8 Alkaline manganese with phenolic 63C	-9	*	*	*	*	*	*	*	*
P.3.8 Standard alkaline manganese 74B				+	+	+	+	+	+
P.3.8 Standard non-alkaline manganese 74D									

specimens flowed, became thermoplastic

\*Too brittle to test.

+Specimens stretched out during exposure - Not testable.

TABLE X  
CHANGE IN PROPERTIES OF MIL-S-83430 B 1/2 (63A) AFTER VARIOUS EXPOSURES

Condition	% Weight Change	Hardness	% Change	Tear Strength	% Change	Tensile Strength	% Change	Elongation	% Change
Initial	---	58	---	80	---	388	---	333	---
7 days JRF @ 140°F	+5.7	38	-35	60	-25	220	-43	425	+28
30 days JRF @ 140°F	+5.5	36	-38	69	-14	207	-47	440	+32
7 days Dist. H <sub>2</sub> O @ 140°F	+9.6	43	-26	64	-20	210	-46	360	+8
30 days Dist. H <sub>2</sub> O @ 140°F	+31.0	30	-48	25	-69	107	-72	275	-17
24 hours @ 360°F	-21.0	92	+59	Brittle					
72 hours @ 360°F	Brittle								
24 hours @ 300°F	-6.2	68	+17	77	-4	457	+18	192	-42
72 hours @ 300°F	-10.8	78	+34	78	-4	484	+25	50	-85
72 hours @ 275°F	-6.0	69	+19	92	+15	456	+18	165	-50
7 days @ 275°F	-8.0	75	+29	80	---	443	+14	75	-78
7 days JRF @ 140°F + 7 days @ 140°F dry	-6.0	68	+17	92	+15	528	+36	175	-48

TABLE XI  
CHANGES IN PROPERTIES OF POLYTHIOETHER/ALKALINE  
MANGANESE WITH PHENOLIC (63C) AFTER VARIOUS EXPOSURE

Condition	% Weight Change	Hardness	% Change	Tear Strength	% Change	Tensile Strength	% Change	Elongation	% Change
Initial	---	25	---	52	---	245	---	700	---
7 days JRF @ 140°F	+17.0	13	-48	42	-19	122	-50	370	-47
30 days JRF @ 140°F	+16.0	10	-60	21	-60	109	-56	370	-47
7 days Dist. H <sub>2</sub> O @ 140°F	+19.0	23	-8	56	+8	165	-33	460	-34
30 days Dist. H <sub>2</sub> O @ 140°F	+74.0	7	-72	25	-52	70	-71	300	-57
24 hours @ 360°F	-5.0	42	+68	32	-38	71	-71	50	-93
72 hours @ 360°F	-9.0	62	+148	Brittle					
24 hours @ 300°F	-2.0	30	+20	51	-2	275	+12	300	-57
72 hours @ 300°F	-2.75	38	+52	45	-14	200	-18	125	-82
72 hours @ 275°F	-2.0	33	+32	46	-12	287	+17	250	-64
7 days @ 275°F	-2.6	37	+48	38	-27	219	-11	160	-77
7 days @ 250°F	-1.7	37	+48	35	-33	280	+14	250	-64

TABLE XII  
CHANGES IN PROPERTIES OF POLYTHIOETHER NON-ALKALINE MANGANESE (740)

Condition	% Weight Change	Hardness	% Change	Tear Strength	% Change	Tensile Strength	% Change	Elongation	% Change
Initial	---	29	---	31	---	267	---	400	---
7 days JRF @ 140°F	+16.0	15	-48	21	-32	86	-68	257	-36
30 days JRF @ 140°F	+16.0	12	-59	14	-55	85	-68	313	-22
7 days Dist. H <sub>2</sub> O @ 140°F	+7.0	22	-24	33	+6	144	-46	517	+29
30 days Dist. H <sub>2</sub> O @ 140°F	24.0	15	-48	23	-26	104	-61	497	+24
24 hours @ 360°F	Thermoplastic								
72 hours @ 275°F	-1.1	24	-17	51	+64	245	-8	367	-8
7 days @ 275°F	-2.0	22	-24	41	+32	147	-45	350	-13
7 days @ 250°F	-1.6	27	-7	37	+19	240	-10	400	---

TABLE XIII  
CHANGE IN PROPERTIES OF POLYTHIOETHER  
SCAVENGED/NON-ALKALINE MANGANESE (74C) AFTER VARIOUS EXPOSURES

Condition	% Weight Change	Hardness	% Change	Tear Strength	% Change	Tensile Strength	% Change	Elongation	% Change
Initial	---	52	---	40	---	310	---	135	---
7 days JRF @ 140°F	+14.0	39	-25	18	-55	150	-52	130	-4
30 days JRF @ 140°F	+13.0	33	-37	19	-53	127	-59	130	-4
7 days Dist. H <sub>2</sub> O @ 140°F	+7.0	46	-12	45	+13	260	-16	225	+67
30 days Dist. H <sub>2</sub> O @ 140°F	+16.0	37	-29	36	-10	245	-21	235	+74
24 hours @ 360°F	-5.0	29	-44	19	-53	50	-84	50	-63
7 days @ 275°F	-1.9	36	-31	44	+10	228	-26	225	+67
7 days @ 250°F	-1.4	42	-19	44	+10	370	+19	260	+93

TABLE XIV  
CHANGE IN PROPERTIES OF POLYTHIOETHER EPOXY CURE WITH PHENOLIC (630)

Condition	% Weight Change	Hardness	% Change	Tear Strength	% Change	Tensile Strength	% Change	Elongation	% Change
Initial	---	43	---	62	---	438	---	350	---
7 days JRF @ 140°F	+9.4	18	-58	38	-39	200	-54	460	+28
30 days JRF @ 140°F	+10.0	24	-44	30	-52	220	-50	370	+6
7 days Dist. H <sub>2</sub> O @ 140°F	+3.8	25	-42	54	-13	285	-35	500	+43
30 days Dist. H <sub>2</sub> O @ 140°F	+7.1	33	-23	50	-19	231	-47	410	+17
24 hours @ 300°F	-2.5	47	+9	16	-74	230	-48	90	-74
72 hours @ 300°F	-3.9	57	+25	17	-73	251	-43	50	-86
72 hours @ 275°F	-2.9	43	---	21	-66	308	-30	100	-71
7 days @ 275°F	-3.4	52	+21	19	-69	249	-41	50	-86
7 days @ 250°F	-1.7	50	+16	14	-77	316	-28	100	-71

TABLE XV  
CHANGE IN PROPERTIES OF POLYTHIOETHER  
EPOXY CURE WITH PHENOLIC (63B) AFTER VARIOUS EXPOSURES

Condition	% Weight Change	Hardness	% Change	Tear Strength	% Change	Tensile Strength	% Change	Elongation	% Change
Initial	---	50	---	41	---	392	---	200	---
7 days JRF @ 140°F	+15.0	31	-38	16	-61	180	-54	170	-15
30 days JRF @ 140°F	+15.0	31	-38	20	-51	160	-59	170	-15
7 days Dist. H <sub>2</sub> O @ 140°F	+3.4	42	-16	32	-22	214	45	250	+25
30 days Dist. H <sub>2</sub> O @ 140°F	+6.5	41	-18	33	-20	200	-49	220	+10
24 hours @ 360°F	-3.8	63	+26	Too Brittle To Test					
72 hours @ 360°F	-7.8	75	+50	Too Brittle To Test					
24 hours @ 300°F	-1.7	51	+2	21	-49	313	-21	125	-38
72 hours @ 300°F	-2.2	53	+6	16	-61	234	-40	50	-75
72 hours @ 275°F	-1.7	53	+6	25	-39	311	-21	100	-50
7 days @ 275°F	-2.0	53	+8	26	-37	250	-36	60	-70
7 days @ 250°F	-1.4	52	+4	25	-39	365	-7	100	-50



TABLE XVI  
CHANGE IN PROPERTIES OF POLYTHIOETHER  
ALKALINE MANGANESE (748) AFTER VARIOUS EXPOSURES

Condition	% Weight Change	Hardness	% Change	Tear Strength	% Change	Tensile Strength	% Change	Elongation	% Change
Initial	---	32	---	47	---	272	---	400	---
7 days JRF @ 140°F	+18.0	14	-56	18	-62	100	-63	307	-23
30 days JRF @ 140°F	+19.0	10	-69	12	-74	100	-63	300	-25
7 days Dist. H <sub>2</sub> O @ 140°F	+24.0	17	-47	25	-47	100	-63	415	+4
30 days Dist. H <sub>2</sub> O @ 140°F	+55.0	7	-78	12	-74	64	-76	377	-6
24 hours @ 360°F	-4.3	29	-9	Brittle					
7 days @ 275°F	-2.3	34	+6	42	-11	275	+1	242	-40
7 days @ 250°F	-1.1	33	+3	38	-19	309	+14	325	-19
7 days JRF @ 140°F + 7 days @ 140°F dry	-6.6	34	+6	54	+15	276	+2	450	+13
7 days Dist. H <sub>2</sub> O @ 140°F + 7 days @ 140°F dry	-0.9	32	---	41	-13	255	-6	450	+13

TABLE XVII  
CHANGE IN PROPERTIES OF POLYTHIOETHER SCAVENGED  
ALKALINE MANGANESE CURE (74A) AFTER VARIOUS EXPOSURES

Condition	% Weight Change	Hardness	% Change	Tear Strength	% Change	Tensile Strength	% Change	Elongation	% Change
Initial	---	56	---	47	---	360	---	120	---
7 days JRF @ 140°F	+16.0	41	-27	17	-64	151	-58	113	-6
30 days JRF @ 140°F	+16.0	37	-34	18	-62	157	-56	127	+6
7 days Dist. H <sub>2</sub> O @ 140°F	+15.0	43	-23	45	-4	251	-30	183	+53
30 days Dist. H <sub>2</sub> O @ 140°F	+46.0	33	-41	20	-57	152	-58	177	+47
24 hours @ 360°F	-4.9	43	-23	39	-17	71	-80	50	-58
7 days @ 275°F	-2.2	48	-14	52	+11	340	-6	140	+17
7 days @ 250°F	-1.0	52	-7	50	+6	494	+37	200	+67
7 days JRF @ 140°F + 7 days @ 140°F dry	-4.7	58	+4	62	+32	412	+14	160	+33
7 days Dist H <sub>2</sub> O @ 140°F + 7 days @ 140°F dry	-6.0	56	---	49	+4	385	+7	---	---

Conclusions from the results in Tables I thru XVII are as follows.

- A. The water resistance, as measured by weight increase, after 30 days in 140°F water is superior with epoxy cures and nonalkaline manganese dioxide cures to that of the control, Thiokol based MIL-S-83430 sealant, as well as the alkaline manganese dioxide cure of the thioether.
- B. The heat resistance, as measured by weight change, is superior with all P-3 formulations at all times and temperatures to that of Thiokol based MIL-S-83430 Sealant. The retention of elongation after exposure to heat was better with P-3 formulations cured with manganese dioxide than with epoxy resin and is better than with Thiokol based MIL-S-83430 sealant.
- C. The fuel swell of P-3 formulations examined is higher than with MIL-S-83430 Sealant.
- D. In fuel exposure, the urethane modified P-3 (P-3U) with phenolic showed an increase in elongation in contrast to a decrease shown by the other polymers. This resulted in higher tear strength values than the other formulations except for the phenolic modified manganese cure which also had high elongation.

VII FACTORS INFLUENCING ELECTRICAL RESISTANCE OF POLYTHIOETHERS IN AEROSPACE APPLICATIONS

One potential application for polythioethers is in electrical molding and potting compositions which require both fuel and water resistance.

Adequate strength requirements should be obtainable if the hydroxyl functional materials are converted to isocyanates and cured with aromatic amines.

Two polymers were compared in this respect, one containing 29% sulfur, the other 38%. Compositional formulas were as follows:

	<u>P-3 (29) %S</u>	<u>P-3 (38) %S</u>
Polymer 2000 equivalent weight	100	100
Toluene diisocyanate	7.5	7.5

Degas & heat together  
until OH group is gone

Methylene dianiline	10.0	10.0
---------------------	------	------

#### Properties

Shore A hardness	94	95
Tensile Strength	2100 psi	1950 psi
Elongation	300%	250%
Tear (die C)	450 pli	350 pli
Volume Resistivity	$1.2 \times 10^{10}$ ohm cm	$1.5 \times 10^{15}$ ohm cm
Surface Resistivity	$7.4 \times 10^{10}$ ohms	$1.3 \times 10^{13}$ ohms

The initial low resistance values of P-3 (29 %S) formulations could not be explained on the basis of structure.

When the P-3 (29) and P-3 (38) materials are prepared, P-3 (29) uses a phosphorous acid type catalyst while the P-3 (38) also uses sulfuric acid. If these catalysts are left in the polymer, low electrical resistance will result.

To illustrate this the P-3 (29) material was heated with MgO and filtered. Before neutralization the volume resistivity was  $3 \times 10^9$  ohm cm. After removal of the phosphorous acid the volume resistivity obtained was  $4 \times 10^{12}$  ohm-cm, essentially similar to the "clean" P-3 (38)

#### VIII URETHANE ELASTOMERS AS FUEL TANK COATINGS

##### A. Physical Properties

The good physical properties of the P-3 urethanes suggests development as fuel tank liners to spray in place integral fuel tanks as well as for repair of fuel bladders. The materials show much higher hydrolytic stability than the currently used polyester urethane products used for fuel resistant bladders.

A comparison of the properties of a typical material with that of a polyester are shown:

Comparison of Polythioether 29% S Isocyanate  
Terminated and Cured with Methylene Dianiline  
With a Polyester Currently Used in Fuel Bladders

	<u>Polythioether</u>	<u>Polyester (commercial)</u>
Tensile	2,000 psi	3,500 psi
Elongation	180%	500%
Hardness Shore D	50	40
After exposure to water at 160°F for 365 days	no change	Reverts to liquid in 10 to 30 days

B. Discussion of Factors Affecting Fuel Resistance:

The substitution of oxygen by sulfur improves fuel resistance over the range of compositions investigated. An overriding effect is the pendant methyl content. Thus a 43% sulfur containing polymer with no oxygen but, a high methyl content is inferior to a 29% sulfur material with 14% oxygen and low methyl content. The difference is clearly the  $\text{CH}_3$  level. The benefit of omitting the oxygen is illustrated by comparing the 29% sulfur material with the 48% sulfur material see Table XVIII. Here the omission of oxygen and increase of sulfur gives materials with improved fuel resistance.

Comparisons of the hydrocarbon fuel resistance of each of the materials was also qualitatively carried out by using isooctane tolerance of the uncured liquid polymers. The relative fuel resistances were in the same order.

METHOD I 5 ml of test polymer were placed in a vial and isooctane added drop wise with stirring until a cloud appeared. The quantity of isooctane required to cause the cloud is an inverse measure of fuel resistance.

METHOD II An equal volume of isooctane and test polymer were shaken in a vial and allowed to stand. The volume swell of the polymer layer was taken as an indication of fuel resistance.

C. Effect of Sulfur Content on Fuel Resistant Mercaptan Terminated Polythioether

A series of hydroxy terminated polymers was available with sulfur contents ranging from 24% to 50%. In order to maintain fluidity, all of the polymers, which were basically repeating units of thioethanol and/or thiodiethanol, contain methyl groups to varying degrees. The composition of these polymers is shown in the accompanying chart:



Table XVIII

Comparison of JRF Resistance in Relation  
to Composition of Backbone

			% Fuel Absorption JRF 1 Week at 120°F of Isocyanate Cured Difunctional Molecule
<u>% Sulfur</u>	<u>% Oxygen</u>	<u>Ratio CH<sub>2</sub>: CH<sub>2</sub>CH<sub>2</sub></u>	
24	12	1.0	40
29	14	0.15	15
43	0	1.0	30
48	0	0.5	9
49	0	0.33	6

D. Water Resistance - Relation to Structure:

A series of uncured hydroxyl and SH mercaptan terminated polymers having between 24% and 49% sulfur with oxygen varying from 14% to 0% was exposed to room temperature distilled water for various periods of time. The time for the polymer to show initial whitening was some indication of water resistance. Permeability to distilled water of isocyanate cured polymers was also determined. All OH terminated polymers were cured with toluene diisocyanate. The following results were obtained:

TABLE XIX

Comparison of Water Resistance  
in Relation to Composition of Backbone

<u>Polymer</u>	<u>% Sulfur</u>	<u>% Oxygen</u>	<u>% Carbon</u>	<u>Uncured Polymer Time to Whiten In Distilled Water At Room Temperature</u>
SH Terminated (Thiokol)	39	19.3	36.1	4 hours
SH Terminated	29	14.4	48.6	4 hours
OH Terminated	29	14.4	48.6	30 minutes
OH Terminated	37	6.2	46.1	1 hour
OH Terminated	24	12.1	54.5	4 hours
SH Terminated	43	0	48.6	>24 hours
SH Terminated	47	0	44.4	>24 hours
SH Terminated	50	0	42.5	>24 hours
OH Terminated (Polypropyleneglycol)	0	27.5	62.0	10 minutes

In general as the carbon content increases, the water resistance increases.

As oxygen increases water resistance decreases.

For comparison a sulfur free polyether is shown as reference.

Note: These values can be improved significantly by removing the catalyst.

The OH termination also affects whitening rate.

TABLE XX

TABULATION OF THE CHEMICAL RESISTANT PROPERTIES  
OF  
MODEL FORMULATIONS OF SULFUR CONTAINING POLYMERS

Polymer	Cure	Basic Monomer Composition	<u>Water Resistance</u>		<u>Fuel Resistance</u>	
			Water Immersion 1 week at 180°F Weight Gain	Water Vapor Transmission gms/m <sup>2</sup> /day @ RT	JRF Absorption 1 Week @ 140°F	JRF Transmission gms/m <sup>2</sup> /day @ RT
Thiokol (38% S)	MnO <sub>2</sub>	Formaldehyde, chlorhydrin sodium polysulfide	10%	20.5*	8.6%+	52
Permapol P-3 (29% S)	MnO <sub>2</sub>	Thiodiglycol and hydroxy ethyl, 2-hydroxy propyl sulfide	5.0%	22,* 30	14.0%	55
Permapol (43% S)	MnO <sub>2</sub>	Mercaptopropanol	1.5%	10,* 16	20.0%	45
Permapol (48% S)	MnO <sub>2</sub>	Thiodipropanol and dimer- captodiethyl sulfide	2.0%	19.6	12.0%	44
Permapol (49% S)	MnO <sub>2</sub>	Reaction product of dimer- captodiethyl sulfide and one mole of propylene oxide	2.0%	23.6	9.2%	49

\* Formulated for water resistance.

+ Formulated for fuel resistance.

Table XXI  
Table Summarizing Fuel, Water, and Heat  
Resistance of Permapol Polymers and Thiokol  
Cured with MnO<sub>2</sub> and Pigmented with CaCO<sub>3</sub>

Material	JRF Vapor transmission gms/sq meter/day	Water Vapor transmission gms/m <sup>2</sup> /day @ 140°F	JRF Weight gain 7 days 160°F	Weight Loss 3 days 360°F
Permapol P-3 (48% S)	44.4	19.2	11.4	16.0
Permapol P-3 (48% S) pigmented exactly like Thiokol that passes MIL-S-8802	39.2	18.0	11.3	20.3
Thiokol formulation that passes MIL-S-8802	51.7	20.5	8.7	Reverted 24 hrs
Permapol P-3 (49% S)	49.0		10.4	
Permapol P-3 (43% S)	45.3	16.2	20.8	12.2
Permapol P-3 (43% S) pigmented with Al trihydrate			10.8	

TABLE XXII  
TABLE COMPARING ENVIRONMENTAL RESISTANCE OF  $MnO_2$  CURED AND PEROXIDE CURED P-3 (29% S)

	WEIGHT CHANGE		TENSILE STRENGTH		ELONGATION		NOTCH TEAR STRENGTH		HARDNESS	
	ALKA. $MnO_2$	HYDRO * PEROXIDE	ALKA. $MnO_2$	HYDRO PEROXIDE	ALKA. $MnO_2$	HYDRO PEROXIDE	ALKA. $MnO_2$	HYDRO PEROXIDE	ALKA $MnO_2$	HYDRO PEROXIDE
Initial	---	---	320	290	300	300	44	40	43	40
7 days @ 250°F	-1.2%	-3.0%	410	300	350	320	50	35	38	34
7 days @ 140°F Dist. Water	+16%	+6%	170	190	370	250	35	30	31	38
7 days @ 140°F JRF	+19%	+13.2%	110	110	310	160	15	25	18	26

NADC-87071-60

Test conducted using 50 phr Calcium carbonate.

\* 2,4 Dimethyl Hexane, 2,4 dihydro peroxide, dispersed in an alkyl ether capped polythioether, with no terminal reactivity.

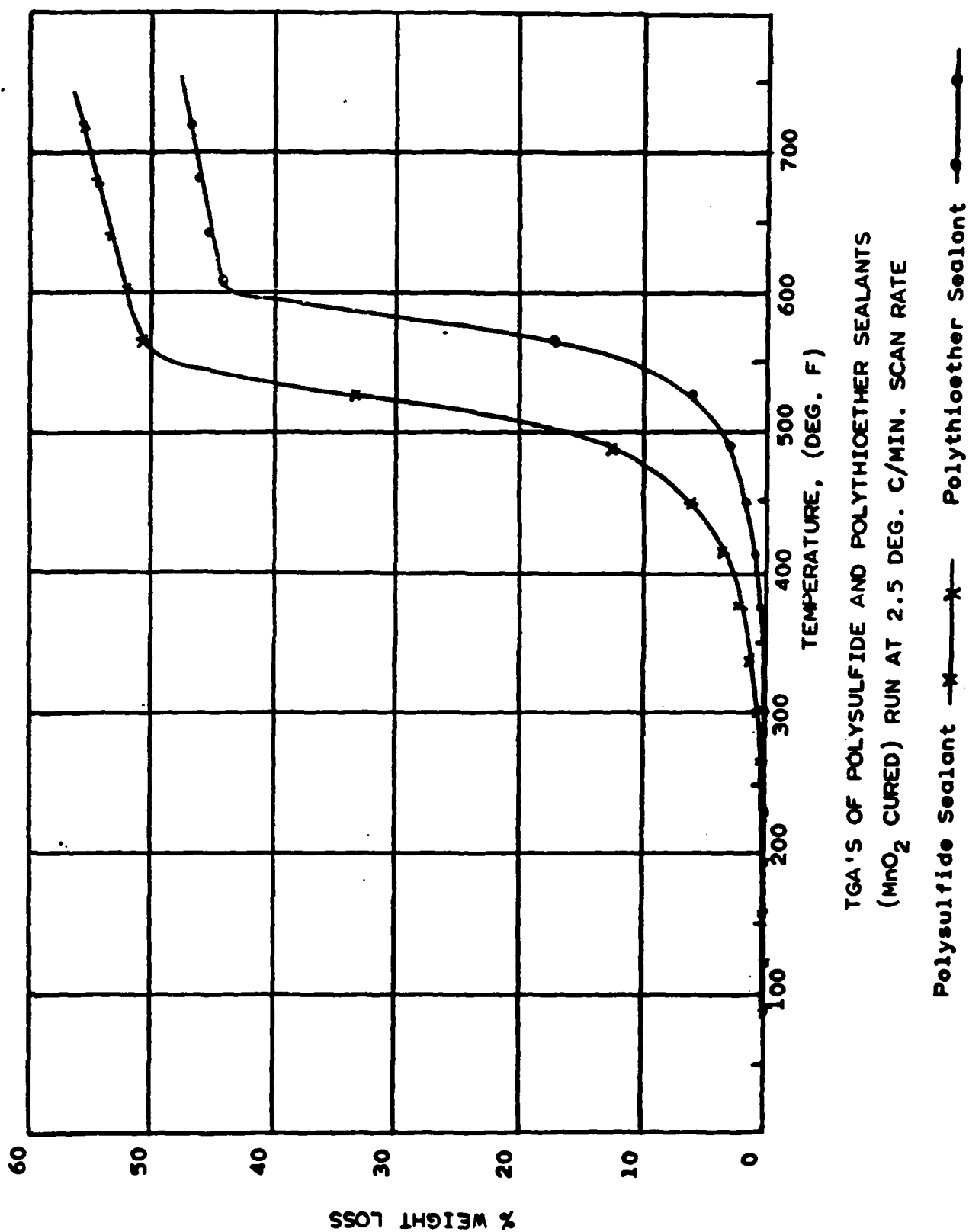
As shown in Table XX, the 43% sulfur material has excellent water and acid resistance as do the higher sulfur analogues. While the fuel resistance of P-3 (43% S), due to the presence of a high percentage of pendant methyl groups is lower than P-3 (29% S), the water resistance is greatly improved.

In Table XXI, it is seen that the use of hydrated alumina lowers the fuel absorption of P-3 (43% S) by one half making it as good as the calcium carbonate pigmented 49% sulfur material.

Early work with polythioether polymers when compared with Thiokol polysulfide polymers using differential thermal analysis showed a significant benefit of the polythioether over the polysulfide in thermal resistance.

See accompanying TGA charts of a polysulfide and polythioether sealant.

Since the potential thermal advantage of the polythioethers could be one of its most valuable properties, a major effort was made to more completely define and demonstrate this advantage.



## IX HEAT RESISTANCE OF POLYTHIOETHERS

A major part of the investigation was devoted to examining the potential heat resistance of polythioethers modified by various curing agents and additives. Preliminary trials were carried out to explore this potential; 2, 4 dimethyl hexane, 2, 4 dihydroxy peroxide was used as curing agent for P-3 (29), mercaptan terminated in place of alkaline manganese dioxide. Comparison of the two materials after exposure is shown in table XXII.

The water and fuel resistance of the cured elastomers was superior with hydroperoxide. The heat resistance, at 250°F however, was somewhat diminished.

A calcium dichromate cure of pigmented P-3 (29) gave a Shore A hardness of 70. After 4 days exposure to 350°F, the material had dropped in hardness to 55 Shore A. There was no sponging. The surface had crusted slightly. In contrast commercial polysulfides survive no longer than eight hours under these conditions.



A triacrylate cure of P-3 (43% S) was made using an amine catalyst. The clear, uncompounded material showed no visible change after 5 days at 350°F except for yellowing. After 8 hours at 400°F, only yellowing was observed. After 24 hours at this temperature softening had occurred, but the product was still elastomeric. Immersion in JRF for one week at 158°F showed a fuel swell of 30% and a definite weakening of the uncompounded material. Nevertheless, the acrylic cure seemed to offer promise of providing a significantly higher temperature resistant material than can be produced with manganese dioxide converted polysulfide. The initial effort to cure the polythioether with acrylic ester is compared with manganese dioxide cured polysulfide and the polythioether in Table XXIII.

A standard Thiokol based formulation qualified to MIL-S-8802 was tested according to MIL-S-83430 along with a Permapol® polythioether formulation containing 29% sulfur and 14.5% oxygen in the polymer backbone. Both materials were cured with manganese dioxide, using a buffered manganese dioxide with the Permapol polymer. An acrylic ester cure is included for further comparison. The following results were obtained:

TABLE XXIII  
COMPARISON OF RESISTANCE OF ACRYLIC CURES OF  
POLYTHIOETHER AND A STANDARD POLYSULFIDE

<u>Physical Properties</u>	<u>Standard 8802 polysulfide MnO<sub>2</sub> Cure</u>	<u>Permapol P-3 (29% sulfur) MnO<sub>2</sub> Cure</u>	<u>Permapol P-3 (29% sulfur) acrylic ester cure</u>
Initial (2 days RT + 1 day 140°F)			
Tensile PSI	459	529	211
Elongation (%)	425	375	180
Hardness, Rex	48	58	55
JRF Immersion (14 days @ 140°F)			
Tensile, PSI	315	289	
Elongation (%)	250	275	
Hardness, Rex	44	41	
Immersion above plus 3 days @ 140°F + 7 days @ 250°F			
Tensile, PSI	286	501	
Elongation (%)	60	250	
Hardness, Rex	69	44	
Heat Exposure-8 hours @ 360°F			(18 Hrs. @ 360°F)
Tensile, PSI	308	385	218
Elongation (%)	60	200	100
Hardness, Rex	69	44	55
8 hours @ 400°F			(38 Hrs. @ 360°F)
Tensile, PSI	No elastic	58	162
Elongation (%)	qualities,	100	75
Hardness, Rex	Cracked, brittle	42	50
Hot Water Immersion 14 days @ 200°F			
Tensile, PSI	113	216	200
Elongation (%)	225	175	105
Hardness, Rex	34	42	52
Weight loss, 7 days JRF @ 140°F + 3 days 120°F	8.7%	3.9%	

The use of an acrylic ester to cure Permapol P-3 (29% S) gave initially inferior physical properties to both a manganese dioxide cured P-3 (29% S) and to a standard polysulfide.

It has been noted in preliminary experiments that the polythioether compounds, uncured, appear to be more stable than most cured samples at 360°F. Addition of metal oxides such as iron, manganese, lead or amines quickly produces darkening and embrittlement. Without such additives only a slow yellowing is observed along with a weight loss per day at 360°F of about 5%, but increasing. In order to examine any potential benefit of stabilizing additives, uncured polymer was mixed with various agents and exposed at 360°F for a number of days. Weight loss and changes in appearance were noted. P-3 (43% S) polymer was also combined with acrylic ester curing agent and exposed similarly.

The effect of additives on the thermal stability of a 43% sulfur material was examined. See tables XXIV and XXV.

The polymer was mixed with zinc oxide and stabilizer at 5% by weight of each. Five grams were spread in an aluminum dish and heated 24 hours at 360°F with the following results:

TABLE XXIV  
EFFECT OF ADDITIVES ON WEIGHT LOSS  
OF UNCURED 43% S MATERIAL HEATED 24 HOURS AT 360°F

	<u>% loss</u>
Control (43% S)	5.0
Zinc Oxide	9.3
Zinc Oxide + Agerite White	6.5
Zinc Oxide + Vanox MTI	50.0
Zinc Oxide + Sulfur	8.0
Zinc Oxide + Hydroquinone	21.8
Zinc Oxide + Thiokol	14.4

Each of the samples was also sealed in a glass vial and heated similarly. The Agerite, sulfur, and Thiokol materials turned black and were foul smelling. The Vanox and hydroquinone were hardened and white or brownish.

Another set of stabilizer experiments were made using triacrylate esters to cure a 43% sulfur polymer with the following observed weight losses. No pigments were used.

TABLE XXV  
Weight Loss of Permapol® P-3 (43% S)  
Cured with Trimethylol Propane Triacrylate  
and Various Additives

<u>Weight % Loss at 360°F After</u>			
<u>Additive</u>	<u>4 days</u>	<u>6 days</u>	<u>Appearance</u>
Hydroquinone 2.5%	28.0	42.7	Rubbery
5.0%	40.8	58.4	Oxidized and hard
7.5%	54.1	67.7	Black, hard
Vanox MTI 2.5%	29.3	48.5	Black, softening,
5.0%	30.1	47.2	All hard in 6 days
7.5%	32.1	50.3	
Acrylic ester, 20% less than theory	21.1	37.1	Good rubber, softer
Hydroquinone + Vanox 5% MTI-5%	30.1	50.1	Glassy and hard
No Additive, Control	47.3	---	Brown, harder
Thiokol LP-32 cured with triacrylate	60.0	---	Very low elongation

In Table XXV above, small amounts of hydroquinone and a deficiency of ester gave superior retention of elastomeric properties.

Additional additives were examined for heat stability utilizing the 48% sulfur material cured with triacrylate ester. In the case of pigmented materials, the weight loss is calculated back to pure polymer.

TABLE XXVI  
COMPARISON OF ACRYLIC CURED THIOKOL AND  
A 48% S POLYTHIOETHER IN WEIGHT LOSS AT 360°F

<u>Description of Test Samples</u>		<u>Weight Loss--Days Exposure at 360°F</u>		
<u>Unfilled Polymer</u>		<u>1 day</u>	<u>2 days</u>	<u>3 days</u>
<u>Additive</u>	<u>%</u>			
Kenrich 46B	5	20	22	25
Stanciere 94C	5	8.6	---	29.4
Thermolite 31	5	6.7	11.35	---
Thermolite 31S	5	9.37		
Thermolite 35	5	12.37		26
<u>Pigmented CaCO<sub>3</sub>-120</u>				
<u>per 100 polymer</u>				
Thiokol LP-32		25.9	44.5	
(acrylic cure)				
Permapol P-3 (48% S)		5.7		30
(acrylic cure)				
<u>Pigmented CaCO<sub>3</sub>-50</u>				
<u>per 100 polymer</u>				
Thiokol LP-32		32.8	47.9	
(acrylic cure)				
<u>Pigmented Ultramarine Blue</u>				
<u>100/100 polymer</u>				
Permapol P-3 (48% S)		7.7	16.3	30
(acrylic cure)				

P-3 (48% S) showed less weight loss than Thiokol in all cases, no benefit of the tin stabilizers on weight loss was noted.

Still other series of tests were conducted examining fuel and heat resistance and some property changes of Permapol P-3 (29% S) polymer formulations cured with acrylic and epoxy-acrylic mixtures. See Tables XXVII to XXXIII.

TABLE XXVII  
TABULATION OF FORMULATIONS CURED WITH ACRYLATES

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u>	<u>H</u>	<u>I</u>	<u>J</u>
P-3 (29% S)	100	100	100	100	100	100	100	100	100	100
MgO	50	10	10	10	10	10	10	10	10	10
TiO <sub>2</sub>	10	12.5	10	10	10	10	10	10	10	10
CaCO <sub>3</sub>	15	50	50	25	50		50	50	40	25
Epoxy Silane	1	1	1	1	1					
CuO	2.5									
Al Powder				15					10	
Ferrocene			.4						.4	
Galvinoxyl					.2					
P-3-43 S						2.5		2.5		2.5
Tin Stabilizer						1.0		1.0		1.0
CaCO <sub>3</sub>						50				25
DEN 431	2									
Glycidyl Acrylate										
20 mol % +										
Trimethylol propane										
triacrylate (80 mol %)	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6

TABLE XXVIII  
EFFECT OF HEATING AT 400°F FOR 8 HOURS ON LAP SHEAR VALUES  
OF THIOKOL & P-3 (29) BASED SEALANTS

<u>Formula</u>	<u>Initial PSI</u>	<u>After 8 Hrs PSI</u>	<u>Percent Retained</u>	<u>Observations On Condition</u>
A	212	19.2	9%	Light color, very hard
B	222	38.0	17.1%	Foamed internally, very hard outside
C	196	39	19.9%	Very hard on outside dark also
D	177	63	35.6%	Very light color
E	225	57.8	25.7%	Hard & dark on exposed areas
F	105	45	42.8%	Smelly on interior
G	185	88	47%	Softer and smelly interior
H	155	31	20%	
I	91	101	110%	Very good
J	184	56.5	30.7	
P-3 MnO <sub>2</sub> cure	260	18	7%	Foamed
MIL-S-8802 Thiokol Mod	137	0	0	
MIL-S-83430	245	2	0.8% left.	Rock hard pigmentThiokol

TABLE XXIX  
FORMULATIONS EXAMINING EFFECT OF FERROCENE & ALUMINUM  
ON LAP SHEAR STRENGTH AT 400°F

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
P-3M (29% S)	100.0	100.0	100.0	100.0
TiO <sub>2</sub>	10.0	10.0	10.0	10.0
MgO	10.0	10.0	10.0	10.0
CaCO <sub>3</sub>	35.0	40.0	40.0	40.0
Al 200 Mesh	5.0	2.5	10.0	10.0
Ferrocene	0.25	0.125	0.125	0.125
Zn Dust	--	--	--	15.0

After 400°F for 8 hours Lap Shear values on Alclad.

<u>Formula</u>	<u>Initial Lap Shear PSI</u>	<u>Lap Shear After 8 Hours @ 400°F PSI</u>	<u>Comments</u>
A	170	14	Reverted and bubbled
B	195	16	Reverted and bubbled
C	228	126	Softer
D	211	50	Smelly

A B and D are cured with 80% mole % TMPTA and 20 mole % glycidyl acrylate at equivalence. C was cured with epoxy novalac, Den 431 at equivalence.

A was in 158°F water 3 weeks with no change in hardness observed. D remained 50 Rex after 5 weeks in 158°F water.

The epoxy cure, DEN 431, along with CuO gave very poor property retention in lap shear.

Aluminum powder along with ferrocene gave excellent retention of lap shear values after heating 8 hours at 400°F.

Thiokol formulations were by far the worst, leaving either no residue or just pigment.

The higher the aluminum powder content, the better the lap shear properties. Zinc dust appeared to oppose the benefits of aluminum.

TABLE XXX  
COMPARISON OF FORMULATED PERMAPOL P-3 (29% S)

WEIGHT LOSSES AT 360°F WITH THIOKOL

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u>	<u>H</u>
P-3 (29% S)	100	100	100	100	100	100	100	50
LP 32								50
TiO <sub>2</sub>	5	5	5	5	5	5	5	5
MgO	15	15	15	15	15	15	15	15
Clay	10	20	25	10	15	15	15	15
Fine Al <sub>2</sub> O <sub>3</sub> 3H <sub>2</sub> O	20	20	20	25	25	25	25	25
Coarse Al <sub>2</sub> O <sub>3</sub> 3H <sub>2</sub> O	25	15	10	20	15	15	15	15
Tensile Strength			136	256	204			
Elongation			225	132	162			
Hardness			29	56	47			

G cured with RD 2/TMPTA 50/50 at equivalence.

A,B,C,D, and E cured with 50/50 1,3 butylene glycol diacrylate/TMPTA at equivalence.

F and H cured with 50/50 glycidyl acrylate/TMPTA at equivalence.

Total Percent Weight Loss at 360°F

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u>	<u>H</u>
One day	2.3	2.55	2.62	2.25	2.56	2.87	3.0	23.04
Two days	3.95	3.69	4.21	3.7	3.87	4.55	5.02	30.1



TABLE XXXI  
EFFECT OF PIGMENTATION ON PHYSICAL PROPERTIES,  
INITIALLY AND AFTER EXPOSURE AT 360°F

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u>	<u>H</u>	<u>I</u>
P-3 (29% S)	100	100	100	100	100	100	100	100	100
TiO <sub>2</sub>		10	10	10	10	10	10	10	10
MgO	15	30	30	15	30	20	20	10	15
Clay	50	30	30	15	30	30	10	10	10
Al <sub>2</sub> O <sub>3</sub> 3H <sub>2</sub> O		30						35	
Al 200 mesh				10					5
Fine Al <sub>2</sub> O <sub>3</sub> 3H <sub>2</sub> O			30	15	30	30	20	10	25
Tensile			320	195	276	283	300	184	
Elongation			100	100	125	188	162	162	
Hardness			60	55	53	55	52	43	

After Fuel Immersion - JRF 1 Week at 140°F

Tensile	162	158	130
Elongation	232	150	150
Hardness	39	48	40

Percent of Weight Loss at 360°F

One day	2.32	2.05	1.99	2.46	2.27	2.86	2.48	2.87
Two days	3.25	3.16	3.02	4.08	3.99			
Three days	4.53							
Four days						8.76	6.94	10.5
Five days		7.33	6.68	9.37	11.58			
Six days	8.85							
Seven days					16.5			
Eight days								

E is made with 50/50 glycidyl acrylate/TMPTA at equivalence. All others cured with equivalence of TMPTA.

F, G, and H made with scavenged polymer (no free OH).

E is better rubber than C after 2 days. It is more flexible.

TABLE XXXII  
EFFECT OF PIGMENTATION AND STABILIZERS ON HEAT AND FLUID  
RESISTANCE OF MODEL FORMULAS

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u>	<u>H</u>	<u>I</u>	<u>J</u>
P-3 (29% S)	100	100	100	100	100	100	100	100	100	100
MgO	10	10	15	20	10	20	20	20	15	15
TiO <sub>2</sub>	5	5	5	10	10	10	10	10	10	10
CuO			5			10	10	10		
Al powder	50		25	30		30	30	30		10
Al <sub>2</sub> O <sub>3</sub> 3H <sub>2</sub> O			5	20	25	30	30	30	50	50
CaCO <sub>3</sub> coated		50			25					
CaCO <sub>3</sub> uncoated							10			
Agerite superlite								2.5		

All cured with trimethylolpropane triacrylate.

Total % Weight Loss at 360°F

One day	2.4	2.2	1.5	1.6	2.3	2.2	1.8
Two days	4.1	4.8	2.6	2.6			
Three days	6.3	6.1					
Four days					7.6	6.2	4.6
Five days				5.7	5.7	9.3	5.7
Six days	9.3	14.4	6.9	6.8		9.9	6.9
Seven days	24.8	17.7	8.2	7.9			
Eight days	30.0	21.1					

Weight Loss % at 410°F

After 18 hrs 4.8 4.5

% of Fuel JRF Weight Gain at 140°F

One day	14.3	13.8	14.4	15.3	15.9
Four days	12.5	13.9	14.9	15.7	15.5
Five days	13.3	14.6	15.4	17.0	16.2

% Water Weight Gain At 140°F

One day	6.2	7.0	5.8	5.4	4.5
Four days	10.1	11.6	9.4	9.1	7.5
Seven days	12.4	16.4	11.7	11.1	8.8

**TABLE XXXIII**  
**EFFECT OF CROSSLINKING ON THERMAL AND JRF FUEL RESISTANCE OF POLYTHIOETHER**

	<u>Modifications For High Temperature</u>								
	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u>	<u>H</u>	<u>I</u>
P-3 (29 %S)	100	100	100	100	100	100	100	100	100
TiO <sub>2</sub>		10	10	10	10	10	10	10	10
MgO <sup>2</sup>	15	30	30	15	30	20	20	10	15
Clay	50	30	30	15	30	30	10	10	10
Al <sub>2</sub> O <sub>3</sub> 3H <sub>2</sub> O		30	30	15	30	30	20	45	25
Al 200 mesh				10					5

<sup>1</sup> Accelerator was TMPTA except for E which was 50/50 TMPTA/glycidol acrylate at equivalence.

<sup>2</sup> F, G, H, and I are based on polymer which had low (0.1) crosslinking in the backbone.

	<u>% Weight Loss at 360°F</u>							
One day	2.3	2.1	2.0	2.5	2.3	2.9	2.5	2.9
Two days	3.3	3.2	3.0	4.1	4.0			
Three days	4.5							
Four days						8.8	6.9	10.5
Five days		7.3	6.7	9.4	11.6			
Six days	8.9							
Seven days					16.5			

	<u>Initial Properties</u>						
Tensile psi		320	195	276	283	300	184
Hardness		60	55	53	55	52	43
Elongation %		100	100	125	187.5	162	162

After JRF Fuel Immersion 1 Week at 140°F

Tensile psi	162	158	130
Hardness	40	48	40
Elongation	232	150	150

The following conclusions can be drawn from results in Tables XXX to XXXIII.

Table XXX, replacement of half of the Permapol P-3 with Thiokol causes an eight fold increase in weight loss at temperature.

Table XXXI, the combination of glycidyl acrylate and trimethylol propane triacrylate showed higher weight loss than the triacrylate alone. Scavenged polymers showed better elongation than unscavenged, but weight loss was higher.

Table XXXII, the use of CuO along with high level of aluminum and alumina gave the least weight loss at temperature. Fuel and water resistance did not change appreciably although aluminum and perhaps CuO contributed to somewhat higher water pickup.

Table XXXIII, lower cross-linked formulas showed both higher initial elongation and increased in elongation after fuel. Their heat resistance tended to be slightly lower.

Raw Materials List

Agerite White	R.T. Vanderbilt Co. Inc.
Alumina Trihydrate	Alcoa Aluminum Co. of America
Aluminium Powder	Alcoa Aluminum
Calcium Carbonate	Sturge Chemicals
Calcium Dichromate	Products Research & Chemical
Clay	Burgess Pigment Company
Copper Oxide	SCM Metal Products, SCM Chemicals
Den 431	Dow Chemical
Epoxy Novalac	Dow Chemical
Epoxy Silane	Union Carbide Company
Ferrocene	Aldrich Chemicals
Galvinoxyl	Aldrich Chemicals
Glycidyl Acrylate	Sartomer Company
Hydroquinone	Van Waters & Rogers
Kenrich 46B	Kenrich Petro Chemicals Inc.
Magnesium Oxide	Merck and Company
Manganese Dioxide (ORE) Fine	Diamond Shamrock
Manganese Dioxide ph 10.2	Shepard Color Company
Methylenedianiline	Allied Chemical Company
Methylol Phenol	Union Carbide Company
P-3	Products Research & Chemical
P-3.8	Products Research & Chemical
P-3.8U	Products Research & Chemical
Stanciere 94C	Interstab Chemicals Inc.
Sulfur	H. M. Royal
Thermolite 31	M & T Chemicals
Thermolite 35	M & T Chemicals
Thermolite 315	M & T Chemicals
Thiokol	Morton Thiokol Corporation
Titanium Dioxide	E. I. DuPont de Nemours & Co.
Toluene	Union Oil Company
Toluene Diisocyanate	Mobay Chemical Company
Trimethylol Propane Triacrylate	Sartomer Company
Ultramarine Blue	Aldrich Chemical
Vanox MTI	R.T. Vanderbilt Co. Inc.
Zinc Dust	Gulf & Western Zinc Div
Zinc Oxide	Gulf & Western Zinc Div.
1, 3 Butylene Glycol Diacrylate	Sartomer Company
2, 4, 6 Tridimethyl Amino Methyl Phenol	Rohm & Haas Company
2, Dimethyl Hexane, 2, 4 Dihydroperoxide	Lucidol Div. Wallace & Tiernan

## DISTRIBUTION LIST (contd.)

Report No. NADC-87071-60

	<i>No. of Copies</i>
Wright-Patterson Air Force Base ..... (AFWAL/MLSE) WPAFB, OH 45433	2
Robins Air Force Base ..... (AFLC) (MANCC), GA 31098	1
Grumman Aerospace Corp. .... Bethpage, NY 11714	1
McDonnell Aircraft Co. .... P.O. Box 516 St. Louis, MO 63166	1
General Dynamics Corp. .... P.O. Box 748 Ft. Worth, TX 76101	1
Lockheed Aircraft Corp. .... P.O. Box 551 Burbank, CA 91250	1
Lockheed Aircraft Corp. .... Marietta, GA 30063	1
Rockwell International Corp. .... 201 N. Douglas St. P.O. Box 92098 Los Angeles, CA 90009	1
Northrop Aircraft Corp. .... 1 Northrop Ave. Hawthorne, CA 90250	1
Boeing Military Aircraft Co. .... P.O. Box 3707 Seattle, WA 98124	1
NADC	
(Code 8131) .....	3
(Code 6062) .....	20

# DISTRIBUTION LIST

Report No. NADC-87071-60

	No. of Copies
Office of Naval Technology .....	3
800 Quincy St.	
Arlington, VA 22217	
(1 for ONT-22)	
(2 for ONT-225)	
Naval Air Systems Command .....	7
Washington, DC 20361	
(1 for AIR-31A)	
(2 for AIR-5304)	
(2 for AIR-5304C2)	
(1 for AIR-5111C)	
(2 for AIR-004D4)	
NAVAIRREWORKFAC .....	1
NAS	
Alameda, CA 94501 (Code 340)	
NAVAIRREWORKFAC .....	1
NAS	
Jacksonville, FL 32212 (Code 340)	
NAVAIRREWORKFAC .....	3
NAS	
Norfolk, VA 23551 (Code 340)	
NAVAIRREWORKFAC .....	1
North Island	
San Diego, CA (Code 340)	
NAVAIRREWORKFAC .....	1
NAS	
Pensacola, FL 32508 (Code 340)	
NAVAIRREWORKFAC .....	1
MCAS	
Cherry Point, NC 28533 (Code 340)	
Office of Naval Research .....	2
Arlington, VA	
(1 for Code 1113)	
(1 for Code 11130P)	
Commander Naval Air Force, U.S. Atlantic Fleet .....	2
Norfolk, VA 23511	
(Code 528)	
Commander Naval Air Force, U.S. Pacific Fleet .....	2
NAS, North Island	
San Diego, CA 92135	
(Code 7412)	
Defense Technical Information Center .....	12
Cameron Station, Bldg. 5	
Alexandria, VA 22314	
Wright-Patterson Air Force Base .....	1
(AFWAL/MLSA)	
WPAFB, OH 45433	